J. At. Mol. Sci.
doi: 10.4208/jams.042813.070213a

Vol. **5** , No. 2, pp. 148-155
May 2014

Study on H_3^+ formation by synchrotron radiation

Qiang Zhang[a], Maoqi Cao[a], Xiaobin Shan[a], Yuquan Li[a], Zhenya Wang[b], and Liusi Sheng[a,*]

[a] *National Synchrotron Radiation Laboratory, School of Nuclear Science and Technology, University of Science and Technology of China, Hefei 230029, China*
[b] *Laboratory of Environmental Spectroscopy, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China*

Received 28 April 2013; Accepted (in revised version) 2 July 2013
Published Online 28 February 2014

Abstract. A molecular beam experiment on the formation of H_3^+ has been carried out by using tunable vacuum ultraviolet (VUV) synchrotron radiation. Reflectron time-of-flight mass spectrometer is applied to detect the signal of H_3^+. The ionization energy (IE) of H_2 and the appearance energy (AE) of H_3^+ are determined to be 15.41 eV and 14.61 eV, respectively, by measurements of photoionization efficiency (PIE) curves. Additionally, two most likely H_3^+ formation ways, $(H_2)2 \rightarrow H_+^3 + H$ and $(H_2)_3 \rightarrow H_3^+ + H + H_2$, are discussed by *ab initio* calculations at CCSD(T) and MP2 level with aug-cc-pVQZ basis set and compared with the experimental result. The optimized geometries of species involved in the dissociative photoionization channels are also determined at MP2/aug-cc-pVQZ level.

PACS: 36.40.-c

Key words: H_3^+, photoionization, synchrotron radiation, *ab initio* calculation

1 Introduction

H_3^+ ion was first found by Thomson in 1912 [1]. Subsequently, a lot of experimental and theoretical works have been devoted to the study of hydrogen clusters since they are perhaps the simplest example of molecular clusters [2-12]. It has established that H_3^+ is a very stable molecule having an equilateral triangular structure [3]. Meanwhile, many theoretical works predicted the geometrical structures of various H_n^+ clusters are composed of a triangular H_3^+ core with surrounding H_2 molecules weakly bound to the core [2-6], whereas recent studies showed the energy of H_6^+ cluster with H_2^+ core is lower than

*Corresponding author. *Email address:* lssheng@ustc.edu.cn (L. Sheng)

that with H_3^+ core [7-9]. The H_3^+ ion also plays an important role in the chemistry of interstellar clouds as an efficient protonator of neutral molecular [13]. Given all this interest it is not surprising that H_3^+ has been the subject of numerous theoretical and experimental studies [2, 10, 11]. However, the details of the mechanism for H_3^+ formation from neutral clusters are still unclear and the appearance energy of H_3^+ is also controversial [11, 12].

The H_3^+ ion can be usually generated by two methods. One method is that it can be easily formed by passing electron beam through molecular hydrogen gas [4]. It believes that H_3^+ is produced by ionic-molecular reaction,

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{1}$$

The large exothermicity of 1.72 eV makes this reaction easily occur, and then larger clusters are subsequently formed in the reaction between H_3^+ and its neighboring neutral molecule. These ionic hydrogen clusters have already been found which included not only the odd-membered ionic clusters but also the even-membered ionic clusters in 1986 by Nicholas and Michael [4]. The other method does not via the ionic-molecular reaction. The ionic hydrogen clusters are formed by ionization of the neutral clusters in a supersonic expansion beam. For example, H_3^+ can be produced by dissociative photoionization of the neutral cluster H_4. The first observation of cluster formation in free jet expansion was by Becker et al. [14] in 1956. They observed the intensities, velocities and speed ratios of H_2, N_2, and Ar beams with changing stagnation temperatures and pressures. Then a lot of experiments for neutral hydrogen clusters have been extensively explored [11, 12, 15-17]. They are almost detected using electron impact ionization mass spectrometers. Because of the unavoidable fragmentation and other disadvantages, such as the appearance energies of fragments obtained in this ionization method is inaccurate [12], photoionization is considered a more accurate measurement in studying of hydrogen clusters. Anderson et al. [11] has carried out the hydrogen cluster research with a light source of a capillary discharge lamp. However, because of the low light intensity, they hardly picked any of the anticipated small autoionzation "peaks" out of the base line in the photoionization efficiency curves of H_3^+ and the AE of H_3^+ they obtained is 0.39 above the theoretical value.

To determine AE of H_3^+ and to explore the mechanism for its formation, we carried out a molecular beam study of H_3^+ using tunable vacuum ultraviolet synchrotron radiation as ionization source for its great advantage. The IEs of H_2, AE of H_3^+ are measured by the PIE curves. Furthermore, with the help of ab initio calculations, two most likely dissociative photoionization channels, $(H_2)_2 \rightarrow H_3^+ + H$ and $(H_2)_3 \rightarrow H_3^+ + H + H_2$, are discussed, and the theoretical IE of H_2, AE of H_3^+ are obtained. In addition, geometry optimizations are also obtained by Gussian 09 at the MP2 levels with the aug-cc-pVQZ basis set.